University of Gondar

College of Natural and Computational Sciences

Department of Chemistry

Spectroscopic Studies of Natural Gem- Agate in Sedimentary and Volcanic host rocks from (Bellesa, Addis zemen and Bure), in Amhara National Regional State (Ethiopia)

By: Belaienesh Tesfa Denkayhu

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Co-adviser: Kumlachew Zelalem Walle (M.Sc.)

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of

Master of Science in Chemistry (Inorganic)

June 2017

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Thesis Approval Sheet

The thesis titled "Spectroscopic Studies of Natural Gem- Agate in sedimentary and volcanic host rocks from (Bellesa, Addis zemen and Bure), Amhara National Regional State (Ethiopia) " by Ms. Belaienesh Tesfa Denkayhu is approved for the degree of "Master of Science in Chemistry (Inorganic)".

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External examiner	

DECLARATION

I, the undersigned, declare that the work reported herein represents my own ideas in my own words and wherever others' ideas or words have been included, I have adequately cited and referenced the original sources. I understand that non-adherence to the principles of academic honesty and integrity, misrepresentation/fabrication/falsification of any idea/data/fact/source will constitute sufficient ground for disciplinary action by the University and can also evoke penal action from the sources which have not been properly cited or acknowledged.

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Signature

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Name of Student

_____

Date

ACKNOWLEDGEMENT

I feel honored to express my gratitude to my adviser Dr. Walelign Wubet and my co-adviser Mr. Kumlachew Zelalem without their consistent supervision, crucial remarks, valuable suggestions and unreserved cooperation the project work and the preparation of the thesis would not have been completed. Their support and encouragement from the beginning up to the completion of this study is kindly appreciated.

I am thankful to Department of Chemistry, University of Gondar, for providing laboratory facilities and materials throughout my study. I would like to thank Debretabor Polytechnique College, South Gondar Administrative Zone, Debretabor; Bahir Dar Polytechnique College, Bahir Dar for the kind donation of the natural gem agate samples. I also acknowledge Ato Hailu Kebede, Gondar Polytechnique College, Gondar, for the kind donation of the natural gem agate sample and for his technical assistance and respectful cooperation in supplying physical property measuring devices to measure refractive index, hardness, and specific gravity of the samples.

Special thanks to Dr. Yonas Chebude, Addis Ababa University, Chemistry Department, for his technical assistance in measuring the samples spectral data using Fourier transform infrared (FTIR) spectrometer. My special shanks goes to Dr. Negash Getachew Addis Ababa University, Chemistry Department for his technical assistance in measuring the samples spectral data using X-ray Powder Diffraction (XRD) spectrometer. Special thanks to Gondar University for their kind cooperation in using the AAS instrument. I would like to express my deepest gratitude and thanks to Mr. Tilahun Belaienesh from Gondar University, Chemistry Department, for his technical assistance in measuring the AAS data of the samples.

Finally I am highly indebted to my colleagues in University of Gondar who had been helping me during my study.

Belaienesh Tesfa

June 2017

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ACRONYMS

FAAS	Flame Atomic Absorption Spectroscopy
FT-IR	Fourier Transform Infrared Spectroscopy
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma- Mass Spectrometry
NG	North Gondar
NGA	North Gondar Agate
SG	South Gondar
SGA	South Gondar Agate
WG	West Gojam
WGA	West Gojam Agate
XRD	X-Ray Diffraction
XRF	X-Ray Florescence
P-XRD	Powder X-ray Diffraction

ABSTRACT

The representative samples of gem-agate were collected from Bellesa (North Gondar), addis zemen (South Gondar) and Bure (West Gojam). The samples were identified and characterized by different physical property measuring devices and advanced spectroscopic techniques. In order to verify that the samples were indeed agate a refractometer, heavy liquid method and "MOHS HARDNESS PENCILS" were used. The performed physical analysis shows that the hardness value of Addis zemen and Bure are in the range of 6.5-7 and that of Bellesa is 7 while the refractive index and specific gravity of both agate samples are similar and in the range of 1.53-1.54 and 2.4-2.7 respectively. The XRD and FTIR spectral data of agate samples from three zones of the Amhara National Regional state have a significant contribution in their identification and characterization. The content of different trace elements (Ca, Mg, Fe, Cu, Cd and Mn) was analyzed by FAAS technique. Generally the investigated agate samples by using FT-IR show a broad band around 4000-2500 cm^{-1}, for the O-H stretch of water molecule is around 3440 cm^{-1} , around 3585 cm^{-1} structural defect of silanol group and around 1084 cm^{-1} for Si-O stretch and at low frequency 694 cm^{-1} indicates the O-H stretch of silanol group. An agate yielded P-XRD pattern is characterized by four broad reflections, the sharp and most intense diffraction peak is pointed at $2\theta = 26.65°$, medium intense sharp peak at $2\theta = 20.00^o$, 24.00^o and 50.14^o, broad peak at 20.83^o and 68.85^o and there is also weaker reflection band occur around $2\theta = 55^o$ and 64.00°. The results are in line with the literature data. The XRD pattern for the three samples from three localities (Bellesa, Addis zemen and Bure, Ethiopia) are almost similar and comparable with the results obtained from the previous studies of agate in other countries (Australia, Morocco, India and Turkey).

Keywords: Gemstone; Agate; FTIR; XRD; FAAS; Ethiopia.

1 INTRODUCTION

1.1 Background of the study

In a recent history, mineral resources have a high priority in the Socio-economic development of the world. Naturally, Ethiopia is elegant and blessed with rich mineral resources. Its diverse geology comprises a variety of precious and semi-precious gemstone as well as industrial minerals resources, which offers a great opportunities for mineral prospecting and development [1].

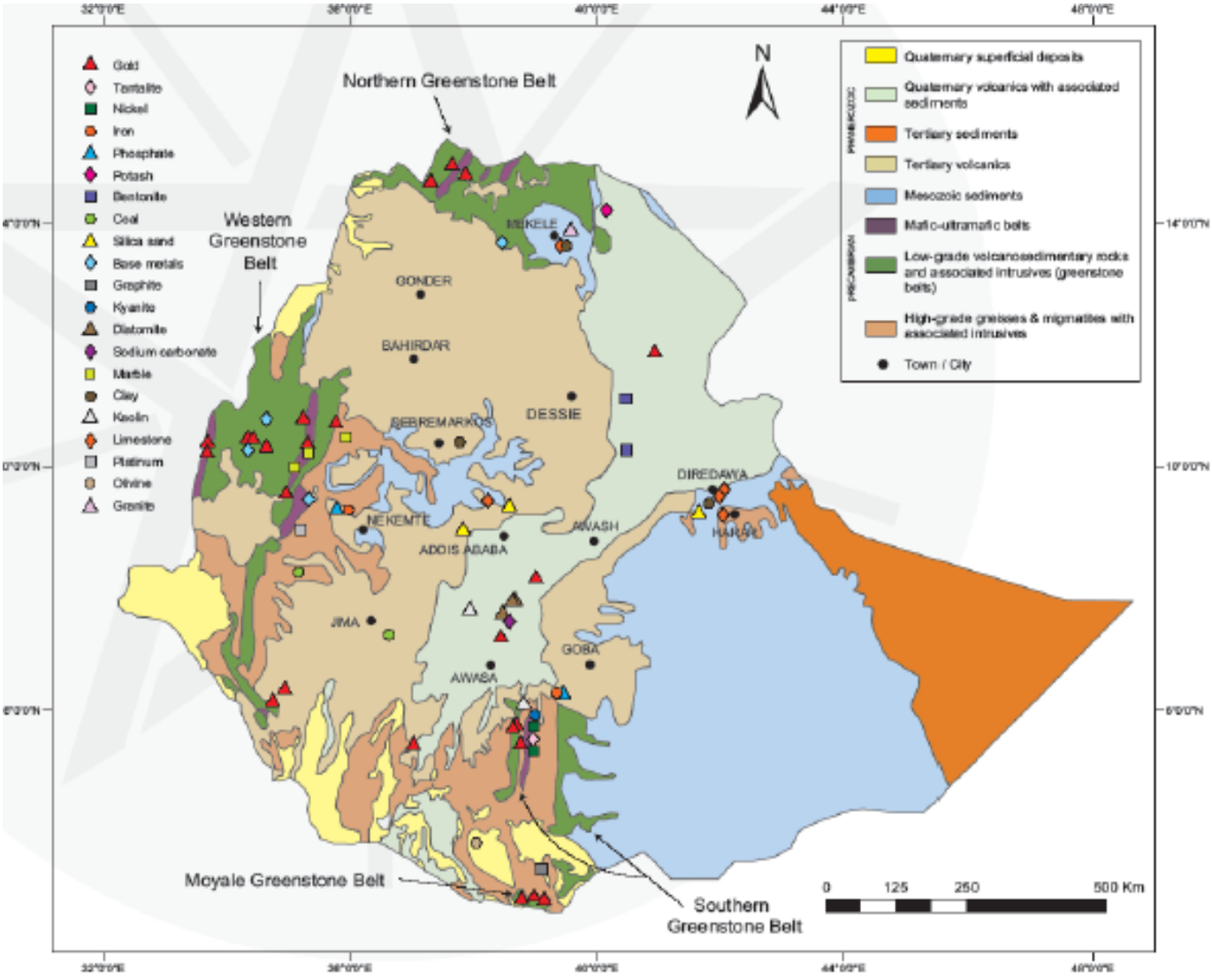

Fig. 1 key mining operations and mineral deposit in Ethiopia [2]

Quartz is the most abundant silica mineral in the earth crust, found all over the world. The mineral potential of Ethiopia lies mainly with the development of gold, potash, thermal energies, and industrial minerals. Some industrial minerals found in Ethiopia are marble, granite, gemstone, limestone, clay, gypsum, iron ore, diatomite, coal, copper, silica etc… [3]

Gemstone

A gemstone is the naturally occurring crystalline form of a mineral which is desirable for its beauty, valuable in its rarity, and durable enough to be enjoyed for generations [4]. Gemstone exploration has recent history in Ethiopia. Quite a few studies were conducted by foreign experts**,** while limited explorations have been done by the ministry of mines besides energy and geological survey of Ethiopia. Gemstone's have higher economic value for the people who deals with it, not only the miners, but also the traders and designers [5].

There are more than 40 popular gem varieties. Some of these varieties have been treasured in early history and others were only discovered recently, almost all of them are found naturally. Gemstones occur in many parts of Amhara and Oromia National Regional States are well known example by their potential resources. Some most common gemstones such as olivine, garnet, Emerald, opal, peridot, beryl, sapphire, jasper, chalcedony, tourmaline, ruby, amazonite, amethyst, obsidian, Agate and petrified wood etc…are found in Ethiopia [6].

Agates are spectacular products of nature, which have a cryptocrystalline structure formed from microscopic particles, mainly fibrous and partially granular silica particles and they are found all over the world including: Asia, Brazil, Germany, India, Italy, Mexico, Nepal, many part of African countries and the USA of different geological environments. They are found in many parts of Ethiopia like Tigray (Adwa, Mekele and Aksum), northern Showa (MehaleMeda, Ankober, Sela Dingay, Jehur, Debre libanose and Yita Mechael), Wollo Kutaber and diverse geological part of Amhara national regional state [6, 7].

Agates are known a unique natural wonder for their amazing colors and different formation patterns, being widely used for jewelry and craft making, which is banded form of finely-grained, microcrystalline quartz. Despite their beauty and popularity, they are mainly composed by silica (a small molecule formed by only few atoms of silicon (Si) and oxygen (O)) with some sort of impurities [8].

Natural gem agate is a microcrystalline quartz mineral, a variety of chalcedony, commonly used in the form of semiprecious gemstones, ornamental objects and grinding media, generally used for best aesthetic purposes [9].

In recent years, the gemstone market has been flooded with stones of questionable origin. Frequently, even thorough analysis by qualified jeweler cannot unequivocally reveal whether a gemstone is genuine or fake. In the worst case, even sophisticated analytical methods struggle to differentiate and examine marketable gemstones.

This paper presents the result of the application of some advanced analytical technique such as X-ray diffraction (XRD), and Fourier transform infrared (FTIR) spectroscopy for discrimination between natural gem agate in volcanic and sedimentary host rocks in Amhara national regional state (Bellesa, addis zemen and Bure) with the other natural gem agate studied by different researchers in different countries (Australia, morocco and Turkey) as well as various trace elements (Ca, Mg, Fe, Cu, Cd, Zn and Mn) in the sample is analyzed by flame atomic absorption spectrometry (FAAS). It would provide more information concerning the real structure of agate and characterize all genetic aspects of natural gem agate in volcanic and sedimentary host rocks in Amhara national regional state (Bellesa, addis zemen and Bure).

1.2 Location and accessibility

The samples were collected from Amhara national regional state particularly North Gondar, South Gondar and West Gojam zones. The research sites are situated at different latitudes, longitudes and elevations. North Gondar zone, specifically Bellesa (has a latitude and longitude of $13^{o}\,12'\,35''N\ 38^{o}\,8'\,25''E$, respectively and an elevation of 2133 meter above sea level), South Gondar Zone, specifically Addis Zemen (has a latitude and longitude of 12°07′N 37°47′E, respectively and an elevation of 1975 meters above sea level) and West Gojjam, specifically Burre (has latitude and longitude $10^{o}\,41'\,59.99''$ N 37° 03′ 60.00″E, respectively and elevation of 2091 meter above sea level).

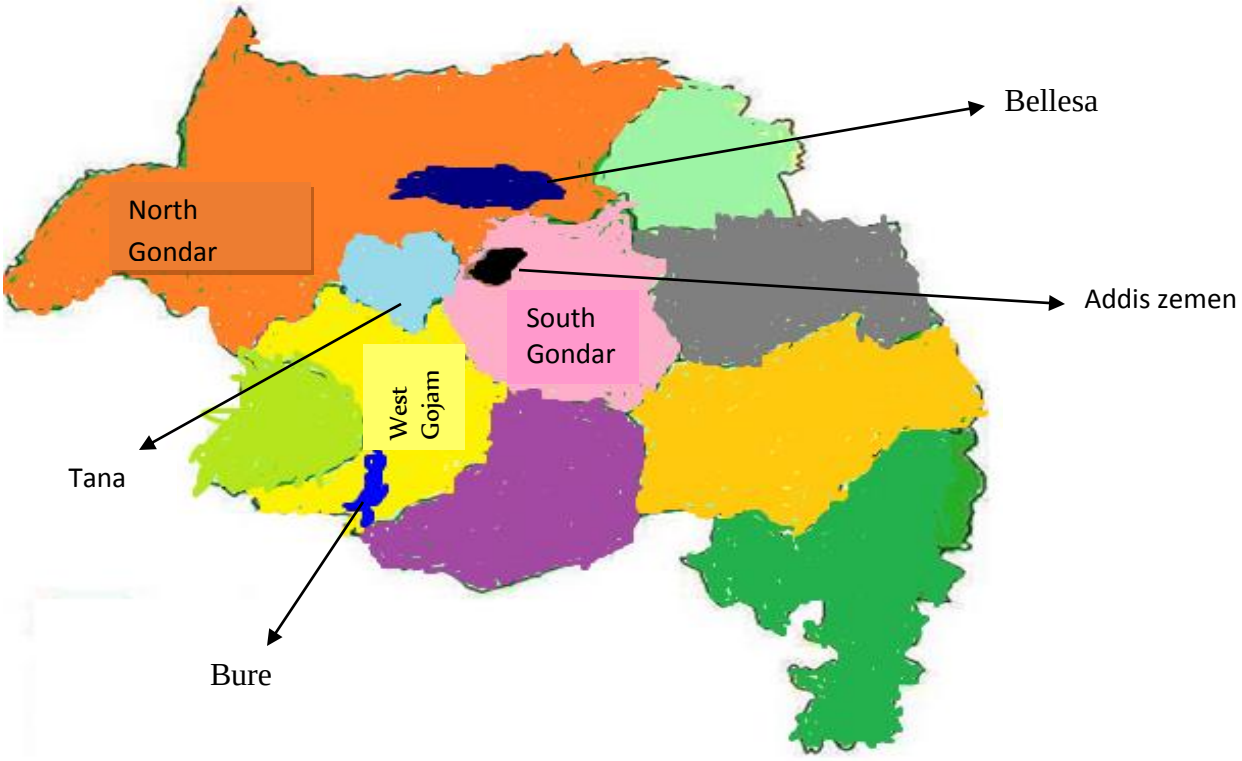

Fig. 2 Sample site location in the amhara national regional state, Ethiopia

1.3 Statement of the problem

There are some challenges to identify and characterize the natural gem agate traditionally, in order to determine the origin, color, composition, hardness, crystalinity and structural defects the sample. It presents the main obstacle that limits when consumers can offer a wide choice of gem material color, quality and prices. In some cases, these materials are sold with incorrect or inaccurate information on their identity. Among these, a few minerals (such like Beryl, Quartz, Topaz, Sapphire, Olivine, Tourmaline, jasper, emerald and Opal) in Ethiopia have been properly studied, identified, quantified and exploited, the remaining require further study. As a result the country has not been able to benefit adequately from its mineral resources. In recent year, though not detail information about natural gem agate hosted in Ethiopia, agates are one of the most important gemstone enthused by consumer and characterized using many advanced spectroscopic techniques. By using these technique I was determine the origin, color, composition and crystalinity and structural defects of the natural gem agate briefly

1.4 Research purpose and scope

Significance of the study

Research findings are necessary for motivating people to contribute some valid knowledge to the society and advancement of the society. The study on gemstone makes hope to standardize in the famous international trade classification and to determine integrity (grading) in the international gemstone trade. Therefore, it is essential to study the identification and characterization of gem agate in order to get accurate and complete information. Disclosure is useful in the jewelry trade to maintain both the commercial value of natural gemstones and the confidence among consumers who are considering gemstone purchases. This study is important for discrimination between natural gem agates hosted in Ethiopia with the natural gem agate in other countries studied by different researchers and also to differentiate natural gem agates from treated and synthetic gem agates using advanced spectroscopic techniques. This study may be useful for the grading of gemstone trade.

1.5 Objectives of the study

General Objective

The general objective of this study is to identify and characterize natural gem-agate hosted in Amhara National Regional State (North Gondar, South Gondar and West Gojam), Ethiopia using spectroscopic techniques.

Specific objectives

The specific objectives of this study are:

- To identify and characterize gem agate hosted in Ethiopia using modern analytical technique (FTIR, XRD and FAAS);
- To identify the order of crystalinity natural gem agate
- To determine its gemological property ;
- To determine the chemical composition of natural gem agate;

- To determine integrity in the international gemstone trade
- To aware the society about the condition of gem agate in volcanic and sedimentary host rocks obtained from (Bellesa, Addis zemen and Bure), Amhara region (Ethiopia) and
- To investigate the practical means of gem identification for jewelers.

Scope of the study

It was very difficult to study on identification and characterization of gem agate in Ethiopia. Identification and characterization of natural gem agate needs a careful investigation by taking long period of time and it requires advanced spectroscopic techniques to identify the chemical composition and structure (such as Raman spectroscopy, ICP-MS and SEM) which were not available in our university. However, this study included some advanced spectroscopic instruments (such as FT-IR, FAAS and XRD) as well as some physical property measuring devices (refractometer, heavy liquid method and "MOHS HARDNESS PENCILS"). Moreover, to conduct this study in three particular zones is too specific and too limited. The result that could be obtained from three zones, but which needed a survey of different zones in the country, will not be comprehensive one.

Limitation of the study:

Some limitations have been occurred to conduct detail study of this research. Namely:

- Shortage of materials, this is to mean that, there are no much studies in relation to the identification and characterization of gem agate.
- Time and budget constrain and
- Some advanced spectroscopic instrument (such as Raman spectroscopy, ICP-MS and SEM) were not available within the university. Then I couldn't determine the composition of oxides (Fe_2O_3, Al_2O_3 …etc.)

2 LITERATURE REVIEW

2.1 The chemistry of agate

2.1.1 Formation and occurrences

Agate is a semi-precious gemstone, which take a wonderful polish and are tough enough for most jewellery uses. Agate is a microcrystalline form of silica (SiO_2). It presents a chemical composition of around 97% of silica and less than 1% of non-volatile impurities. The concentration of impurity from H_2O and Si-OH is up to 2%. Silica in agates is composed by two of its polymorphs: α-quartz and up to 20% of moganite. In 1999, Zoetze *et al.,* presents the structure of agate can probably be interpreted as alternating formation of fine-grained, highly defective chalcedony intergrown with moganite, and coarse-grained low-defect quartz [10].

To explain about how do agates form, several theories are settle down, but basically all of them state that agates form by the systemic deposition of silica in cavity walls generally resulting in banded patterns. The geochemical study demonstrated that the formation of agate can be a complex, multi-steps process. A very simple description of this process is that high temperature, pressure or ionized surface and magmatic waters are capable of dissolving the silica from the rocks where they pass through. When these water flow or evaporate, there is the formation of silica deposition [11].

$$Mg_3Si_2O(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + H_2O \quad \ldots\ldots\ldots\ldots (1)$$

Agates are beautifully colored semi-precious gemstone, which is commonly found in eruptive volcanic rocks or in lavas of the earlier eruption. These agates have banded crystal architecture with successive parallel layers to the side of cavities. These are the feature of cooling magma fluids in the form of bubbles of steam and other gases which overtake the process of solidification and are frozen in cavities. Later the fluid carrying alkali silicate percolates in to these bubbles and triggers coagulation and to become silica jell. Designers often take advantage of the intriguing patterns these stones have to offer to create unique and fascinating pieces [10].

Many agates form in areas of volcanic activity where, water rich in dissolved silica (SiO_2), flow through fractures and cavities in igneous rocks. When the solution is highly concentrated with dissolved silica, a silica gel can form on the walls of these cavities. That gel will slowly crystallize to form microcrystalline quartz. And also agates typically form in igneous rocks such as basalt, rhyolite, and andesite, they can also form in sedimentary rocks such as limestone [12].

Agates are known to be formed in rock cavities. Most of these cavities are gas bubbles or blow holes in volcanic flows formed by the expansive forces of gases and vapors within these rocks when they melt. Other cavities, such as those produced by the decay of wood, are also subject to agate deposition. Theories of formation have been concerned with the manner of deposition of silica in these cavities to produce banding. Generally formation of agates takes place in volcanic rocks, hydrothermal veins or in sediments [13].

In spite of the worldwide occurrence of agate, its genesis has proved an ongoing enigma; the silica source and the repetitive nature of banding need explanation. T.moxon *et al*., in 2006, explained that the origins would either the direct precipitation of chalcedony or the precipitation of amorphous silica, which then evolves into chalcedony. Agates do not form in laboratory time and the method of silica transportation, mode of deposition, temperature and mechanism of crystallization are all problems that have obscured agate genesis [14].

It typically occurs in various volcanic and sedimentary rocks in nearly all countries on earth. Most agates occur in cavities in eruptive rocks or ancient lavas. It is a mineral generally of secondary origin, forming in cavities and veins by deposition from meteoric groundwater containing gelatinous silica from the weathering of silicate minerals [15].

2.1.2 General properties of natural agate

Because of its wide variety of shape, texture and color, Agate is spectacular and famous gemstone [16]. Like a crystal it does not have a homogeneous structure, and it usually not made up of a single type of mineral. It resembles a rock made up of different components in varying proportions [17]. Agates belong to the most fascinating mineral objects in nature because of their wide spectrum of colors and spectacular forms. Agates are in general banded chalcedony with the chemical formula SiO_2 but in detail they may represent a mixture of certain SiO_2 polymorphs

and morphological quartz varieties and naturally agate is a tough, dense material with dull to a waxy luster and conchoidal fracture. It is by far less brittle than rock crystal. Agate is somewhat porous and usually contains small amounts of water [18].

Agates are hard, durable stone which can be dyed easily in sliced very thinly and that can be highly polished. Generally, they are affordable which varies from extremely translucent to opaque [19].The main Physical properties (color, crystal form, hardness, specific gravity, luster, index of refraction and transparency) are important aids in identifying gemstones [20].

A) Crystallography

Agate, mainly built of fibrous microcrystalline alpha quartz with the chemical formula SiO_2. There are some trace quantities of other components that can give agate layers [21]. Agates from flood basalts commonly display repetitive textures and trace element compositions. From rim to core, agates typically consist of three parts: concentric layers of length-fast fibrous chalcedony, an inner layer of coarse length-slow quartz crystals (quartzine), and a central void. However, many agates lack a central void and instead are filled in completely with silica, while others consist only of banded fibrous chalcedony. Agates vary widely in shape, size, and color, but surprisingly their structural and compositional characteristics are relatively constant [22].

B) Hardness

Hardness is the resistance of a mineral to scratching or abrasion by other materials. It is determined by scratching the surface of the sample with another mineral. Scratch hardness defined as the resistance of mineral when scratched with a pointed testing object. The hardness values of agates in Mohs scale ranges from 6.5-7.

Hardness of a gemstone is its resistance to scratching and may be described relative to a standard scale of 10 minerals known as the Mohs scale. (F. Mohs), an Austrian mineralogist, developed this scale in 1822. According to Mohs' scale, the hardness of ten minerals is shown in table below [23].

Table 1. Hardness of some minerals in Mohs' scale

Minerals	Hardness in (Mohs' scale)	Minerals	Hardness in (Mohs'scale)
Talc	1	Feldspar	6
Gypsum	2	Quartz	7
Calcite	3	Topaz	8
Fluorite	4	Sapphire	9
Apatite	5	Diamond	10

C) Specific gravity

Specific gravity is the number of times heavier a gemstone of any volume than an equal volume of water; in other words, it is the ratio of the density of the gemstone to the density of water. The specific gravity of a mineral is the weight of that mineral divided by the weight of an equal volume of water. The specific gravity of natural gem agates are within the range of 2.4-2.7 [24].

D) Cleavage

Cleavage is the tendency of a crystallized mineral to break in certain definite directions, giving more or less smooth surfaces. This splitting is due to weak cohesive forces present in a mineral along different directions and is also related to the form and crystal structure of the mineral. Agates are mostly lacking cleavage and being composed of microscopic sized crystals closely bound together, are often tough, and this has led to the assumption of superior hardness over quartz. The cryptocrystalline varieties have no distinct cleavage; the fracture surface is either sub conchoidal or hackly [25].

E) Refractive index

The refractive index (RI) is of prime importance to the faceted. The amount of refraction in the crystal is constant for each specific gemstone. Therefore, it can be used to identify the types of gemstone. The amount of refraction, refractive index, is defined as the proportional relation between the speed of light in air and that in the stone. The decrease in the velocity of light in the stone causes a deviation of light ray. Refractometer is an instrument used to measure the refractive index of the gemstone (i.e. the refractive index of agate is in the range between 1.530-1.5400) [26].

F) Color

The color is the feature that draws most attention in minerals, which is the most important characteristic of gemstones, because color, or the lack of it, is a major factor in the beauty of gem materials. There are several explanations for the cause of color; some are the effects of white light, chromospheres, all chromatic minerals and transition metal. This is determined by its chemical composition and /or crystalline structure. Agates are characteristically colored, from the practically colorless varieties to grey, pink, and red, orange, blue, green, with predominating brownish-red specimens [27]

2.1.3 Application of gem agate

The different cryptocrystalline varieties of transparent and translucent chalcedony are valued as Semi-precious stones and are carved out into a variety of ornaments and used for making different ornamental wares or articles of decoration. Agate pieces after cutting and polishing are sold as semiprecious stones. This is used for laboratory equipment such as mortar and pestle. And cutting Agates into requisite shapes is also used as fulcra of scientific balances and in making edges, planes and bearings of precision instruments [28].

Agate is a microcrystalline quartz mineral, a variety of chalcedony, commonly used in the form of semiprecious gemstones, ornamental objects and grinding media. Most agates occur as hollow boulders of eruptive rocks or ancient lavas and show a distinctive banded structure of peculiar shape and color, which is not disturbed during crystallization. Successive layers lie

approximately parallel to the rock surface and can be seen in cross sections, generally used for best aesthetic purposes [9].

The most common application of gemstone is jewelry and decorative manner. This gem possession has been reserved for wealthy, royalty or high religious leaders. This gemstone was widely used by the ancient civilizations for embellishing armory, statues and especially in the art of hard stone carving. The first prehistoric civilization that became famous for the use of this gemstone in their jewelry, signet rings, seals and beads was the sumerians. Agate is believed by many to be a stone of strength. It was used by the ancients on the breastplates of armor to give warriors strength and make them victorious in battle. It is also known as a good luck stone. [29].

The decorative arts use it to make ornaments such as pins, brooches or other types of jewellery, paper knives, inkstands, marbles and seals. Agate is also still used today for decorative displays, cabochons, beads, carvings and Intarsia art as well as face-polished and tumble-polished specimens of varying size and origin. Agates have long been used in arts and crafts

2.2 Physical measurements

The Fourier Transform Infrared (FTIR), X-ray diffraction (XRD) and Flame Atomic Absorption Spectroscopy (FAAS) techniques were found to be useful scientific tools in identifying the natural gemstones**.** All of these technique can perform the characterization or qualitative screening through elemental quantification of natural gem agate. It can be used to quantify the elements found in gem-agate as well as other materials that serve as evidence of certain treatment processes [30].

Characterization using ICP

Analyses of the distribution of trace elements and stable isotopes should provide important information concerning the geochemistry of agate and genetic aspects of agate formation. Most of the time agates are occurred in certain volcanic rocks containing some amount of trace elements. These trace elements are detected by using Modern analytical techniques LA-ICP-MS, which is a suitable analytical method for the detection of trace elements in very low concentrations. In 2009, Robert Möckel *et al.*,reported about the measured trace–elements of

agate in Nowy Kościół (Lower Silesia, Poland). The investigated trace-element were: Li, Na, Al, Ge, Rb, Sr, Ba, Y, La, Ce, Eu, Gd, Dy, Ho, Th, U, Ti, Mn and Fe and the results show that most of the measured trace-elements are present in very low concentrations [31].

Another study about the bulk composition trace element analysis of dendritic agate sample obtained from turkey by using (ICP-AES) and XRF studied by Levant. Parali *et al*.,in 2011, presents that dendritic agate is mainly composed of SiO_2 (91.2%) and also abundance of Al_2O_3, Fe_2O_3, CaO and Na_2O within the range of 0.13%, 0.67%, 0.67%, and 0.03%, respectively. Thirty-five elements (Ag, Ba, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Hf, Ho, La, Lu, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sm, Sn, Sr, Ta, Tb, Th, Tl, Tm, U, V W,Y) were measured by (ICP-AES) and XRF, of which 10 are rare-earth elements [32].

Characterization using FTIR

Infrared (IR) spectroscopy was used to assess the water content, the vibrational motion of hydroxyl ions and water molecules present in silica that exhibit characteristic peak absorption bands using IR spectrum. By using this technique, David R .Lee, in 2016, determined two water types present in silica minerals; molecular water and silanol groups. He was used the agate sample obtained from liver pool, which resulted to sharp absorption peaks below 1400 cm^{-1} are recognized as relating to stretching and bending of Si-O bonds, broad absorption bands within the range of 4000-2500 cm^{-1} are due to O-H stretching vibrations and the broad asymmetric band at around 3400 cm^{-1} is due to hydrogen bonded molecular water. A band present between 3750 cm^{-1} and 3500 cm^{-1} has been attributed to SiOH groups, with a notable sharp peak observed at 3585 cm^{-1} is assigned to SiOH located at structural defects [33].

Another researcher Moxon.T*et al*., in 2006, also mentioned the water content of agate investigated from the three sites in Western Australia. by using this technique resulted the broad peak from 4000 to 2500cm^{-1} is due to fundamental O–H stretching vibration and the shoulder at 3585cm^{-1} is assigned to Si –OH at structural defect sites [14].

Agate is cryptocrystalline banded chalcedony. In 2010, Hatipoglu.M,*et al*., presents the (FT-IR) spectrum of blue chalcedony from the Sarıcakaya-Eskisehir region (turkey) using (1330 FT- IR spectrophotometer Perkin-Elmer Company in (USA)). From the result of their experimentation,

they have concluded that spectrum around 695 cm^{-1} indicated the ‘‘OH’’ stretch, 1080 cm^{-1} the asymmetric Si =O= Si stretching, 2910 cm^{-1} Si-O vibration and around 3450 cm^{-1} OH stretching was mentioned [34]. Parthasarathy.G, *et al*., in 2001, also studied about chalcedony/agate from killari, (India) by using modern analytical technique (FT-IR), to compare the FT-IR spectra of moganite-rich and quartz-rich samples (quartz) with that of moganite-rich and chalcedony-rich samples. They thought that the gross features of the IR absorption spectra of moganite and quartz were similar. However, the absolute values of the absorption bands of moganite were distinctly different from those of quartz. Two absorption peaks at 800 and 700 cm^{-1} were present both in moganite and quartz. Strong absorption near 1190, 1105, 808, and 480 cm^{-1}, were due to dominancy of the fundamental vibrations of the tetrahedral SiO_4 spectra. The bands in the region 1200 to 620 cm^{-1} was assigned to Si-O stretching vibrational modes, however, the spectra of chalcedony and moganite were not distinguishable in the frequency region 4000 to 2000 cm^{-1} due to the presence of the similar hydroxyl component in both phases. A very broad absorption band of H_2O was observed at about 3450 cm^{-1} [35].

Characterization using XRD

Levant Parali *et al.* (2011) studied the XRD patterns of the dendritic agate and the results of their experiment showed the sharp and intense diffraction peak at $2\theta = 26.62°$ with the d-spacing value of 3.34 Å and a weak reflection at approximately $2\theta = 65.74°$ with d-spacing values between 1.4193 and 1.422 Å, and a broad peak at $2\theta = 20.83°$ with the d-spacing value of 4.26 Å [32].

T. Moxon *et al*. (2006) studied agate by using XRD spectroscopic techniques of Bruker D8 diffractometer with Cu-Kα radiation. From their study, microcrystalline quartz showed peak broadening at higher 2θ range [14].

Murat Hatipogul *et al*. (2011) investigated Anatolian agates (from Turkey) by using X-ray diffractometer. The result of the study demonstrated that the moganite (Mo) silica phase were present in the overlapped diffraction bands in addition to main chalcedony silica phase (Ch), forming the chalcedonic matrix components in the cryptocrystalline structure of agates. An intense and sharp diffraction peak at $2\theta = 26.615^o$ with d-spacing value of 3.35 Å, a weak peak at $2\theta = 64.01^o$ with d-spacing value of 1.45Å and broad peak at $2\theta = 20.82°$ with d-spacing value of

4.26 Å were observed. Generally the XRD pattern of agate showed eleven resolved peaks at 2θ = 20.82º, 26.615º, 36.525º, 39.455º, 42.43º, 45.75º, 50.12º, 54.85º, 59.94º and 68.25º [36].

3 METHODS AND ANALYSIS

3.1 Instruments, apparatus, reagents and standards

Instrumentation and Apparatus

A refractometer of United Kingdom manufacture was used to measure the refractive index of agate with an optical contact liquid of 1.79 ± 0.05 at 25 ºC. The specific gravity was measured using heavy liquid test (Lithium salt with specific gravity value 2.57 (UK)). Mohs Hardness Pencils (UK) was used to measure the hardness value of agate sample. A diamond pacific machine (UK Manufacture) was used to cut agate sample and a diamond paste machine (UK) was used to polish (clean) the agate sample. The ball mill grinder was used for grinding the agate sample. A sieve with 0.1 mm size was used to sieve powdered agate samples. An electronic digital balance (Denver instrument company USA) was used to weigh the powdered agate sample. Spectrum 65 FT-IR spectrometer (PerkinElmer instrument company U.S.A) was adjusted in transmittance mode and equipped with a 4x beam condenser with resolution 4 cm^{-1} and scanning speed auto (16 mm/sec) in the wave length range of 400 cm^{-1} up to 4000cm^{-1}, was used for recording infrared transmission spectra of agate sample using KBr pellet method.

Miniflux 600 powder diffractometer (Rigaco instrument company, USA) equipped with CuKα radiation (λ = 1.5418 Å) and a scan speed of 1°/min and in the range between 10-70° 2θ was used to collect X-ray powder diffraction data for quantities and semi quantitative analyses of the mineral phase in the agate sample and host rocks.

Borosilicate Erlenmeyer flask and hot plate were used to digest the agate sample. Filter paper was used to distill the digested agate sample. The pipettes (1mL, 2mL, 5mL), 100mL, 50mL volumetric flask, 50mL of Erlenmeyer flask and beakers were used to dilute the standards and samples' solution. An atomic absorption spectroscopy (BUCK SCIENTIFIC MODEL 210 VGP, U.S.A.) equipped with air/acetylene flame, with a hallow cathode lamp for the determination of Manganese, Cadmium, iron, calcium, zinc, copper and magnesium were used.

Chemicals and Standard Solutions

Chemicals that were used in the analysis are analytical grades. Deionized and distilled water was used for cleaning of glassware and for dilution of samples. Ethanol was used for washing the crystal sample after cutting. KBr (obtained in the PerkinElmer (U.S.A) accessories and consumable kit). 48% of HF (Anala R, PARK: Hydrofluoric acid Solution Northampton scientific Laboratory supplies, U.K), 69-72% (Analytical R, IMO: Nitric acid solution BDH Laboratory supplies, England) of HNO_3, 35.38% of HCl (Blulux, Laboratory reagent, Blulux Laboratories (p) LTD-121001), and 30% of w/v H_2O_2 (MS Laboratory Reagent, Medical PVT.LTD, New Delhi) were used to digest the agate samples. Stock standard solution of the metals Ca (1000 mg/L), Fe (1000 mg/L), Mn (1000 mg/L), Mg (1000mg/L), Zn (1000mg/L), Cd (1000mg/L) and Cu (1000mg/L)) prepared for an atomic absorption spectrophotometer (BUCK SCIENTIFIC MODEL 210 VGP, U.S.A.) were used for the preparation of calibration curves for the determination of metals in the samples.

3.2 Procedures

3.2.1 Collection of agate samples

The agate samples were collected from the Polly technique colleges (Gondar, Debretabor and Bihar Dar) in cooperation with Administrative Zone Technical Vocational Enterprise Development Departments of South Gondar Zone, Debretabor; North Gondar Zone, Gondar and West Gojam Zone, Bahir Dar, and these three samples of natural gem agates were obtained from mining.

3.2.2 Determination of gemological properties

The physical properties of the samples were measured in order to verify that the samples are indeed agate or not. These gemological (non-destructive) characterization techniques were performed on representative samples. The physical measurements were performed at Gondar poly-technique College gemological testing laboratory, Gondar in Maraki branch. For these purpose a refractometer UK manufacture was used to measure refractive index (RI) with an optical contact liquid of 1.78±0.05 RI at room temperature and the specific gravity was measured

by heavy liquid method (Lithium salt)."The instruments of MOHS HARDNESS PENCILS" were used to determine the hardness values of agate samples.

3.2.3 Sample preparation

By following the procedure, the natural gem agate samples were washed with distilled water in order to remove surface contamination and dried in sunlight. The samples were cut with a diamond pacific machine and polished by a diamond paste. After that the samples were washed by distilled water, ethanol and dried in air and then grounded in to a fine powder by using ball mill grinder and sieved with a 0.1 sieve.

Sample preparation for FT-IR

The FTIR analysis was carried out by taking powdered gem-agate samples exactly 2mg for each (measured using electronic digital balance) and mixed with 200mg KBr in order to prepare circular pellet.

Sample preparation for XRD

The XRD patterns analysis was carried out by taking powdered natural gem-agate samples and transferred it into sample holder of the instrument.

a) **b)** **c)**

Fig. 3 The natural gem agate samples from (a) North Gondar, (b) South Gondar and (c) West Gojam.

Sample preparation for FAAS

For FAAS analysis, from three powdered agate samples (0.5 g each) was weighed and put in to three replicate 50mL borosilicate glass of Erlenmeyer flask and 5ml conc. 69-72% HNO_3, 2ml 35.5% HCl, 1ml 30%w/v H_2O_2 and 2mL of 48%HF were added. Then after the Erlenmeyer flasks were heated on hot plate and the solution evaporated near dryness. After that 2 mL 48% HF was added and heated for a few times until precipitation of SiO_2 is eliminated as SiF_4 vapors. Cooling down to the room temperature, 2mL conc. HCl and 5 mL of distilled water were added. Finally the solution was transferred in to 250 mL volumetric flasks and filled up with redistilled water up to the mark [34].

3.3 Physical measurements

3.3.1 Characterization using FTIR

Before the samples were run in the spectrum 65 FT/IR spectrometer PerkinElmer (U.S.A), the instrument's total inspection was done by measuring absorbance of the standard polystyrene film and empty sample compartment turn by turn. A background (KBr) measurement was done. Powdered FT-IR spectra was collected at Addis Ababa University on 65 FT-IR PerkinElmer (U.S.A) spectrometer equipped with KBr beam splitter. Approximately 2mg of the sample was weighed using electronic balance and mixed with KBr powder (200mg for each sample).The mixtures were further powdered to mix well and then put in the instrument sample holder for solid sample analysis. Then each sample was examined by spectrum 65 FT/IR spectrometer PerkinElmer (U.S.A) operated at transmittance mode and resolution 4 cm^{-1} and scanning speed auto (4 mm/sec) in the wavelength range of 400 cm^{-1} to 4000 cm^{-1}.

3.3.2 Characterization using XRD

To analyze, three gem-agate samples by using the modern analytical technique of (miniflux 600 powder X-ray diffractometer) Rigaku instrument company U.S.A with rotating copper target of voltage 220v and current 15 A, the fixed mass of powdered agate samples were weighed and transferred into the sample holder of the instrument.

The instrument was adjusted with Cu tube and a graphic monochromator with CuKα radiation (λ= 1.5418Å) and a scan speed of 1°/min in the range between 2θ = 10-70°. The Powdered X-ray diffraction (XRD) experiment was performed at Addis Ababa University in Ethiopia.

3.3.3 Trace metal determination using FAAS

To analyze the agate samples using the FAAS, the instrument were adjusted in appropriate manner such as, wave length selector; hallow cathode lamp, slit width, fuel valve and etc. The absorbance of the analytic line is a function of several parameters, burner head position (vertical, horizontal) and flow rate of used gases. Optimal values of these parameters are those, which yield maximum absorbance value. The optimization procedure was carried out by studying the effect of one parameter while keeping the others constants at appropriate values. To carry out this study the acetylene and airflow rate were kept constant. Before the samples were run in BUCK SCIENTIFIC MODEL 210 VGP, FAA spectrometer, the presence of precipitate in the sample as well as standard solution were refined and total inspection was done by measuring the absorbance of distilled water.

For the determination of metals in both North Gondar, South Gondar and West Gojam agates, five series of standard metal solutions (Table-2) were prepared by diluting the standard solutions of the metal with distilled water. A blank (distilled water) and standards were run in flame atomic absorption spectrophotometer to establish five points of calibration curve. Each Sample solutions were aspirated into the FAAS instrument and direct readings of the metal absorbance were recorded. Three replicate determinations were carried out on each sample. The operating conditions of FAAS employed for each analyte are given below (Table 3).

Table 2. Series of working standards for determination of metals in North Gondar, South Gondar and West Gojam agate varieties using flame atomic absorption spectrometer.

No	Element	Concentration of Standards (µg/ml)	Correlation coefficient (R)
1.	Ca	0.1, 1, 1.5, 2, 2.5	0.992
2.	Zn	0.1, 0.5, 1, 1.5, 2	0.994
3.	Mg	0.5, 1, 1.5, 2, 2.5	0.987
4.	Mn	0.1, 0.5, 1, 1.5, 2	0.919
5.	Fe	1, 3, 5, 7, 9	0.995
6.	Cu	0.1, 0.5, 1, 1.5, 2.5	0.982
7.	Cd	0.1, 0.5, 1, 1.5, 2	0.997

Table 3. Instrumental operating conditions for determination of metals using (FAAS)

Element	Wavelength (nm)	Energy (J)	Slit Width (nm)	Current (mA)	Detection limit (mg/L) from the instrument's operator mnual
Mn	283.2	3.783	0.7	2	0.03
Zn	213.9	3.3	0.7	2	0.005
Mg	285.2	4.529	0.7	1	0.005
Ca	422.9	4.086	0.7	2	0.05
Fe	248.3	3.84	0.2	7	0.05
Cu	324.7	3.839	0.7	7	0.01
Cd	228.8	3.24	0.7	2	0.03

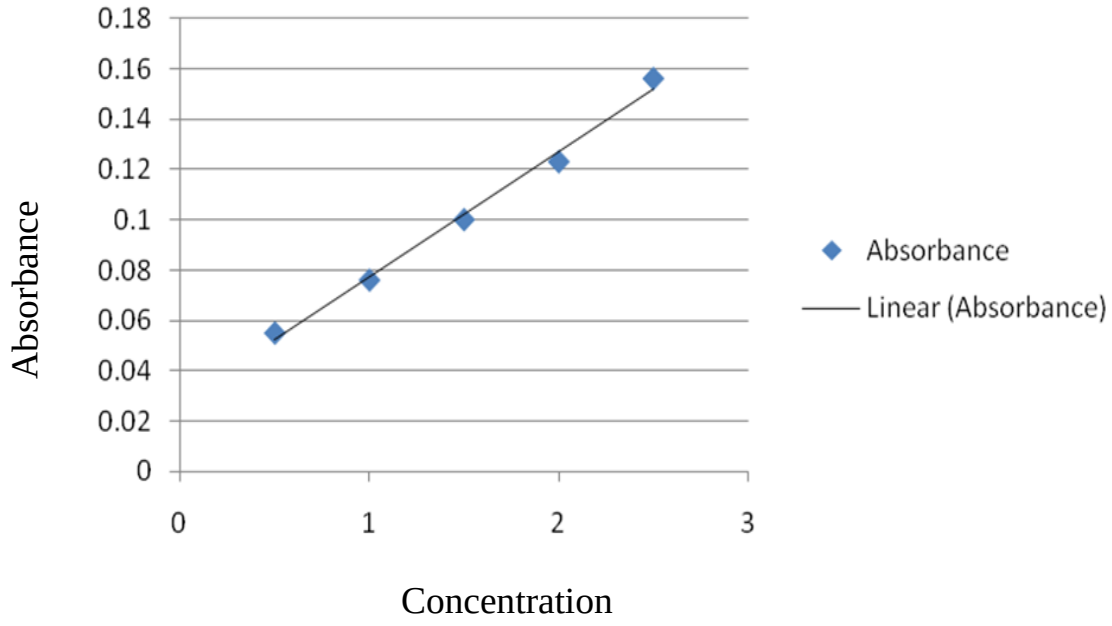

Fig. 4 Calibration graph for calcium standard solution

Y = 0.049x + 0.027

R^2 = 0.992

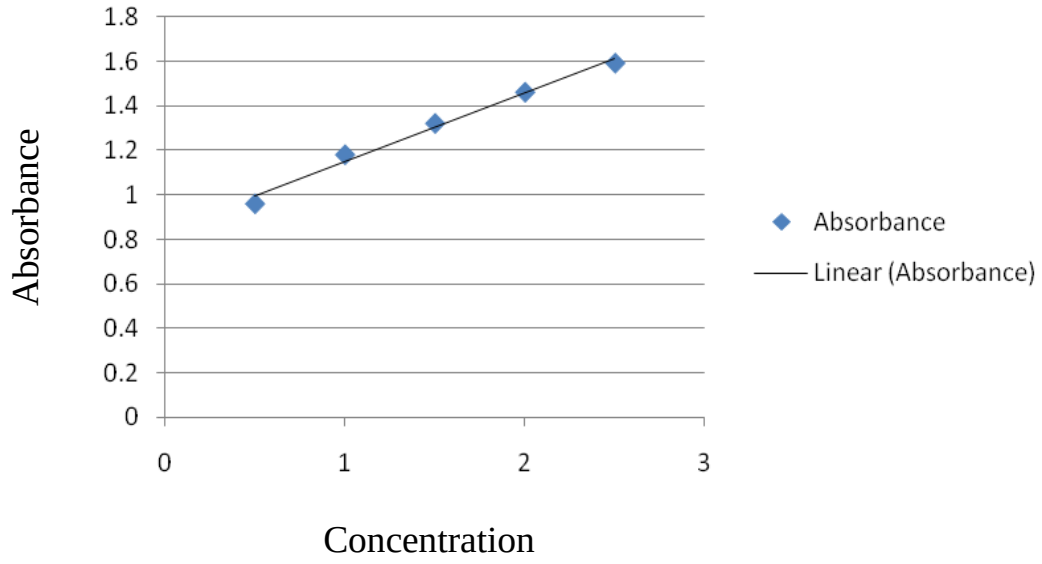

Fig. 5 Calibration graph for magnesium standard solution

Y =0.308x +0.84

R^2 =0.987

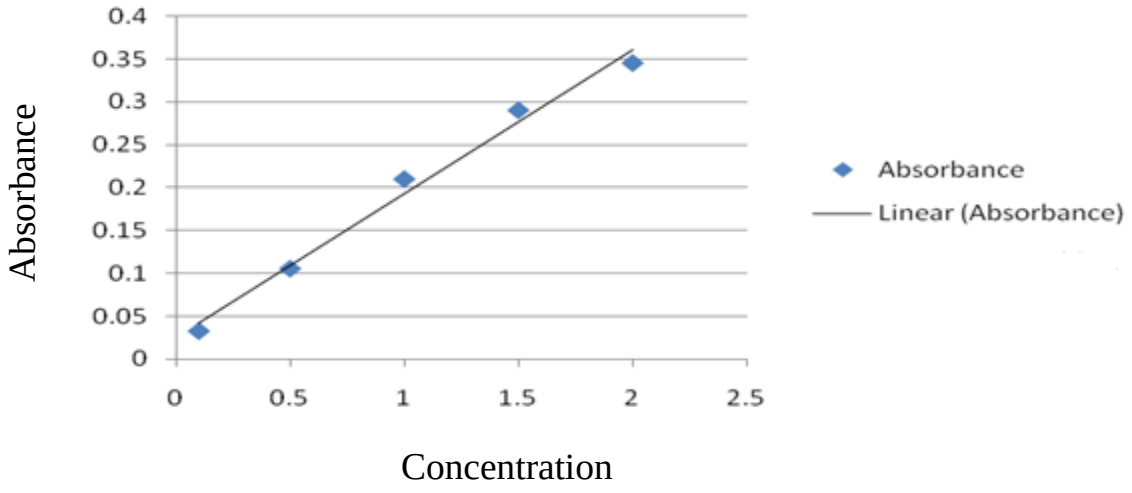

Fig. 6 Calibration graph for manganese standard solution

Y = 0.168x + 0.025

R^2= 0.919

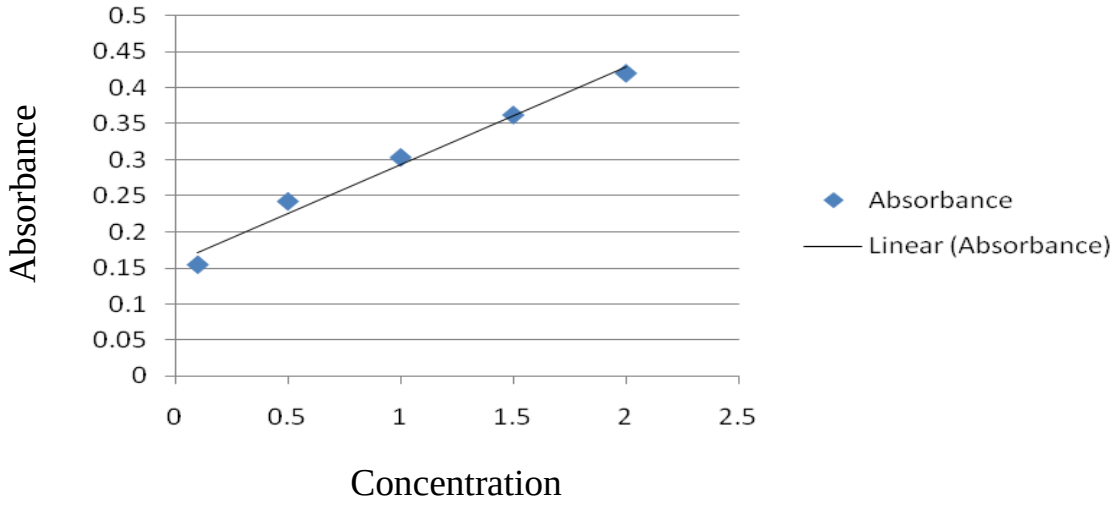

Fig.7 Calibration graph for cupper standard solution

Y=0.135x + 0.158

R^2 = 0.982

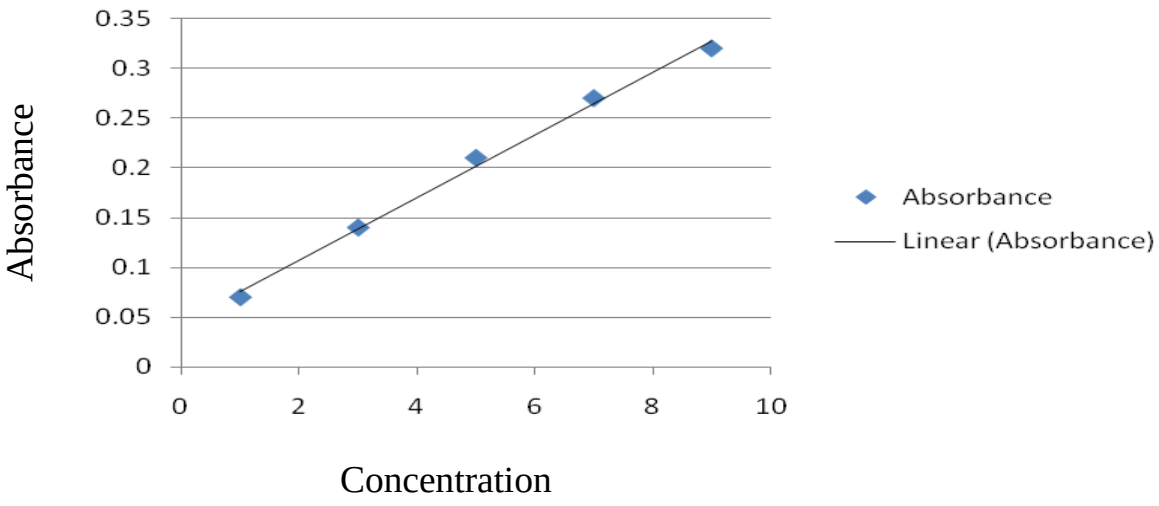

Fig. 8 Calibration graph for iron standard solution

y = 0.031x + 0.044

R^2 =0.995

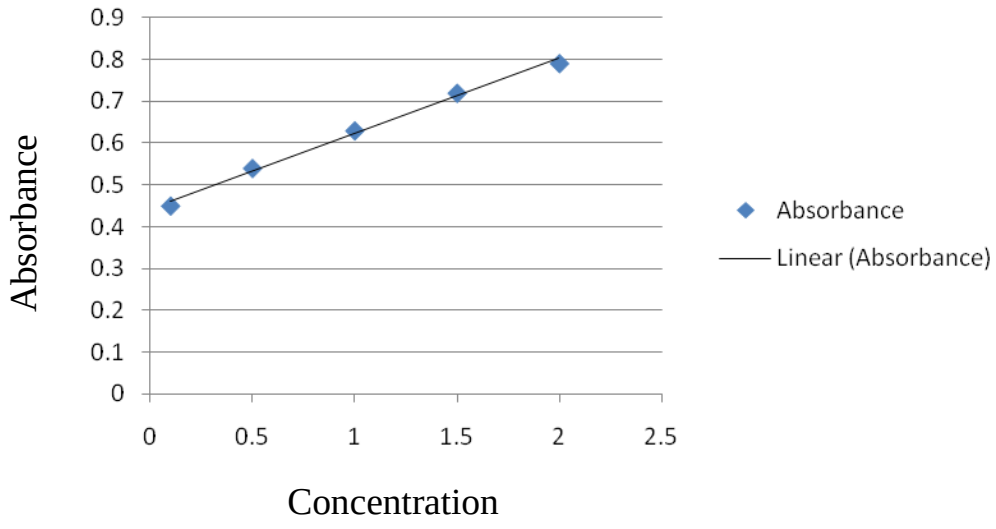

Fig. 9 Calibration graph for zinc standard solution

Y = 0.179x + 0.443

R^2 = 0.994

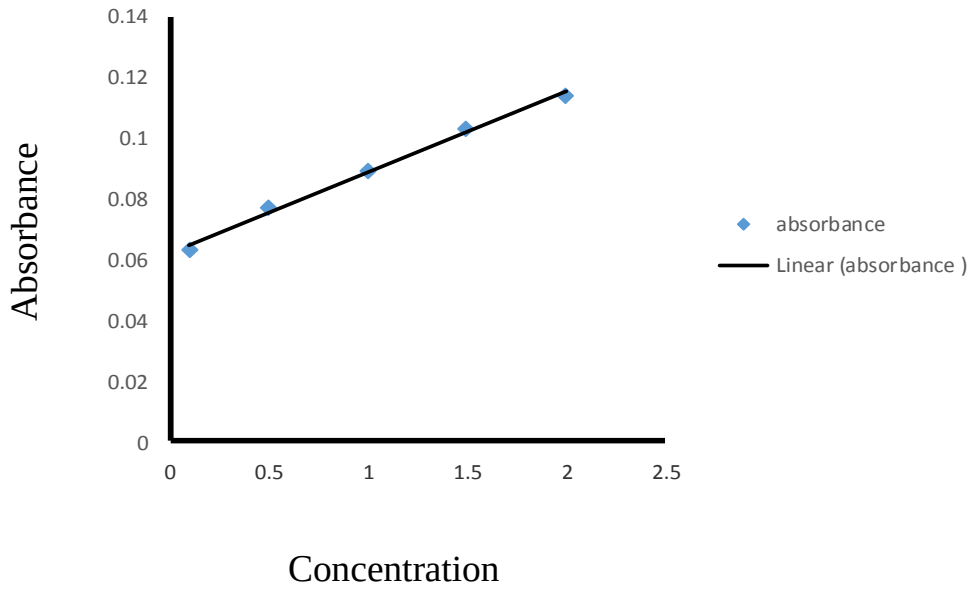

Fig.10 Calibration graph for cadmium standard solution

Y = 0.0266x + 0.0621

R^2 = 0.997

4 RESULTS AND DISCUSSION

4.1 Gemological properties

To verify the investigated natural gem agate samples were indeed agate, non-destructive gemological characterization techniques were performed on representative samples. First, average specific gravity value of representative samples were measured by heavy liquid method using (Lithium salt). The results were within the range of 2.4-2.7. A similar result was observed in [24]. Because of optical character and optical sign, refractive index values of representative samples were determined by using standard refractometer device with an optical contact liquid of 1.79 RI. The refractive index values of the investigated samples were within the range of 1.53-1.54. A similar result were observed in [26].

"The "Mohs hardness pencils" were used to determine the hardness of gem-agate samples. This physical analysis shows that the hardness value of the addis zemen and Bure agates are similar and they were within the range of 6.5-7 and that of Bellesa is 7. Thomas Arter reported that the hardness value of agates are within the range of 6.5-7 [23].

The results of all these gemological testing values indicate that the samples were indeed agate samples. To compare these three sample the natural gem agate obtained from Bellesa is harder but their specific gravity and refractive index are almost similar to that of Bure and addis zemen.

4.2 Infrared spectroscopy analysis

Infrared spectroscopy is dependent on the response of short-range, molecular scale, energetic vibrations such as O-H stretching and bending. This generates characteristic spectra for particular mineral phases depending on the molecules present, for example different water species. The vibration ranges of the hydroxyl (OH) group water species, main silica mineral building components or inclusions, structural point defects, structural bonds, and coloration in silica can be determined using FT-IR spectrum in the mid-infrared region. Therefore, mid-infrared absorption spectroscopy is widely used to reveal the presence of water in gem and other mineral species. Meanwhile, the initial included waters in all mineral species can be divided into three groups, namely the hydroxyl (OH) group located at structural defects, surface hydroxyls hydrogen bonded to each other (H–O–H), and free molecular water (H_2O) [14, 33, 34]. The infrared spectra of Bellesa, Addis zemen and Bure samples are presented in figures 10, 11, and 12 respectively.

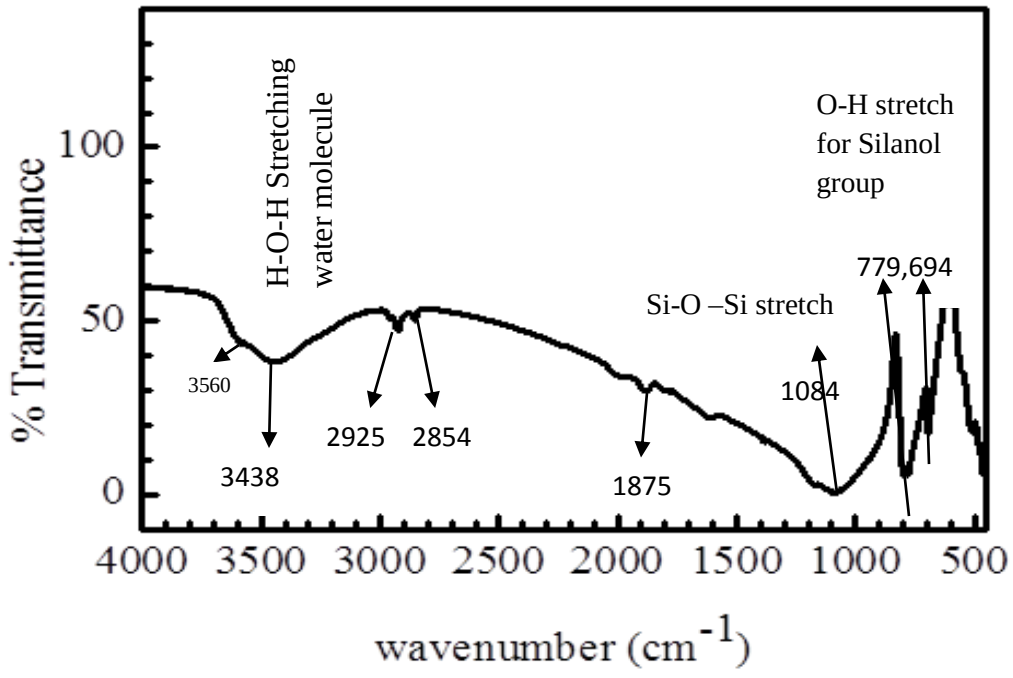

Fig. 11 The FT-IR spectrum of agate sample from Bellesa in north Gondar

The FT-IR spectra of the investigated samples obtained from three different places (Bellesa in NG, Addis zemen in SG and Bure in WG) of Ethiopia were analyzed within the frequency region of 400 to 4000 cm^{-1} (Fig. 11, 12 and 13). The gross features of the FT IR absorption spectra of this three agate samples were similar. However, the absolute values of the absorption bands of Bellesa agate (694, 779, 1084, 1736, 1875, 2854, 2925, 3421, 3430, 3433 and 3438 cm^{-1}) are distinctly different from those of Addis zemen agate (693, 779, 1086, 1874, 1877, 1879, 2718, 3446, and 3576 cm^{-1}) as well as the Bure agate (694, 797, 1082, 1687, 1878, 2924, 2963 3445 and 3586 cm^{-1}). The FT-IR spectra of these three investigated agate samples were characterized by a multi component broad absorption bands centered around 3443 cm^{-1}. This absorption band is related to the OH stretching and vibration in molecular water (H_2O). Similar results were observed in [14, 33, 34].

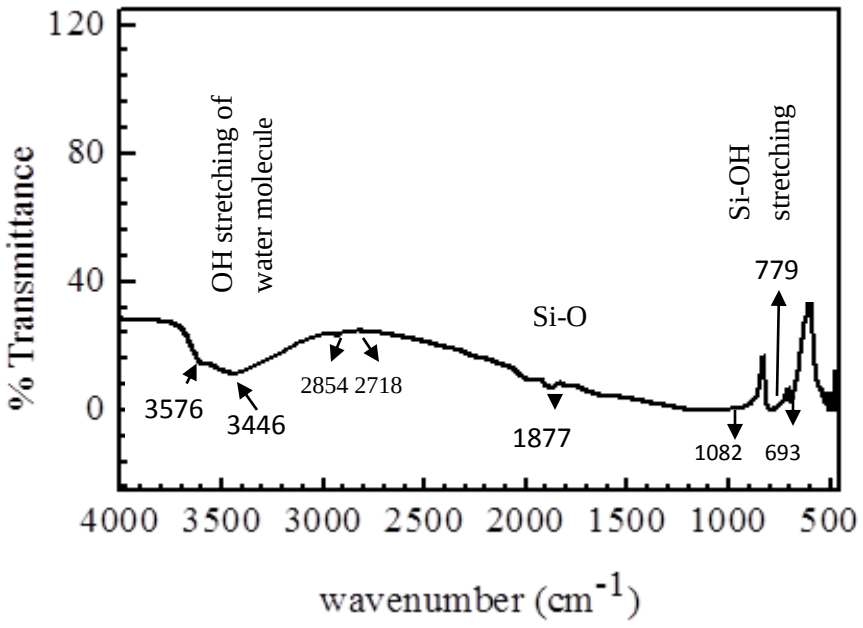

Fig. 12 The FTIR spectrum of agate sample from Addis zemen in south Gondar

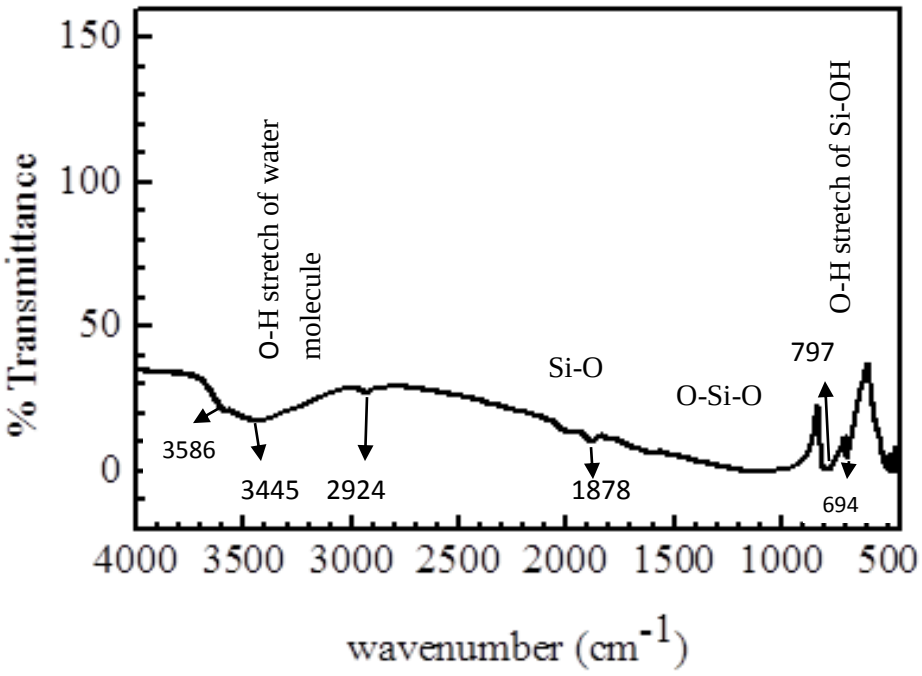

Fig. 13 The FTIR spectrum of agate sample from Bure in west Gojam

According to the study conducted by Moxon T. *et al*. (2007) the sharp band present at approximately 3585–3590 cm^{-1} attributed to the structural defect of silanol (Si-OH) species. This structural defect is either water or hole). The FT-IR spectrum of Bellesa agate (NG),Addis zemen agate (SG) and Bure agate (WG) sample show weak shoulder around 3560, 3576 and 3586 cm^{-1}, respectively, indicating the presence of structural defects of silanol group [14,33].

In the low frequency region, from 1200cm^{-1} - 600cm^{-1}, the investigated samples have three bands centered around 694 cm^{-1}, 779$cm^{-1}$and 1084 cm^{-1}. These bands are due to the fundamental vibrations of SiO_4 tetrahedral, related with Si-O stretching vibration. There were a similar observation in [14, 33, 34, 35]. Particularly, the bands occur around 1080 cm^{-1} are assigned to asymmetric Si=O=Si stretching vibration and a band around 750-800 cm^{-1} is assigned to O-Si-O bending vibration, whereas the band centered near 694 cm^{-1} is assigned to OH stretching vibration of silanol group. The observed data were comparable with literature data [34]. In these investigated samples, the percent transmittance value of Bellesa agate, Addis zemen agate and Bure agate were almost around 60, 29 and 35%, respectively. From this observation one can conclude that addis zemen agate absorbs the IR radiation higher than the other two and Bellesa

agate is transparent to IR radiation in comparison with the other two. From this analytical technique we can generalize the OH stretching and bending vibration of water molecule in the three agate sample assigned to around 3446 and 1687 cm^{-1} respectively, moreover the silanol groups are around 694 cm^{-1} .

Table 4. Assignments of the Fourier transform infrared (FT-IR) bands of the gem-quality Agate from Amhara national regional state of Ethiopia

V(cm^{-1})	Assignment
Around 694	OH stretch vibration's related to silanol
779- 797	O-Si-O bending vibration
1082-1086	Asymmetric Si=O=Si stretching
Around 1687	OH bending of water
1874-1878	Si-O bending vibration
Around 2925	Si-O stretching vibration
3421-3446	OH starching of water molecule
3586	Si-OH structural defects

4.3 Powder x-ray diffraction analysis

Gemological properties and mineralogical composition of natural gem-agate can be identified by different spectroscopic techniques. The mineralogical assemblage of host rocks could be determined by XRD pattern. An X-ray powder diffraction pattern was obtained for a sample of pure agate in three different zones of Amhara national regional state, Ethiopia (Fig. 14, 15 and16 below).

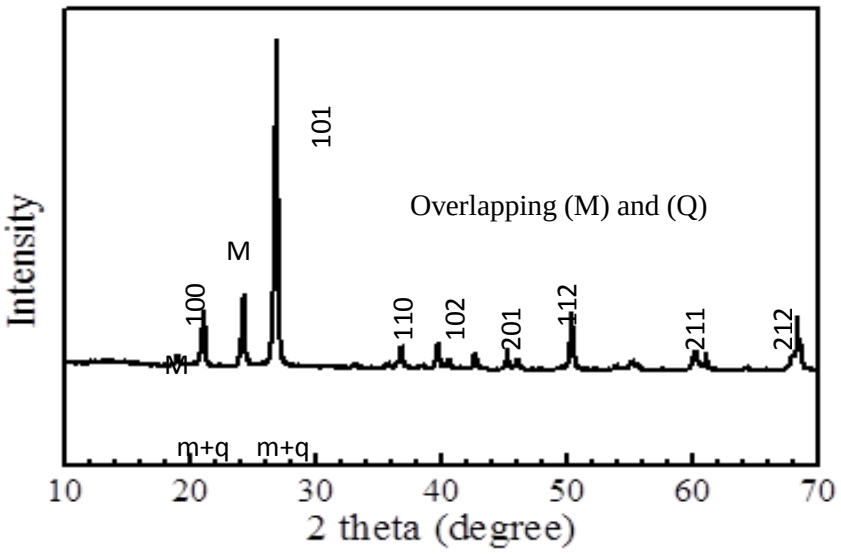

Fig. 14 X-ray diffraction patterns of the (Bellesa agate)

In this study, the investigated natural agate samples in the range between 10° to 70° show some resolved peaks at 2θ = 20.85°, 26.65°, 36.54°, 39.46º, 42.47º , 45.81°, 50.14º, 54.87º, 59.95º and 68.32º. According to the study conducted by Paral L. *et al* and Hatipoğlu M. *et al.* (2011) and Maoxon .T *et al.* (2008) on agate using XRD the same resolved peaks at the same 2θ values were observed. The numerical data obtained from XRD analyses of NGA, SGA and WGA samples were comparable with those studied natural agates of Australia and Turkey origin [14,32, 36].

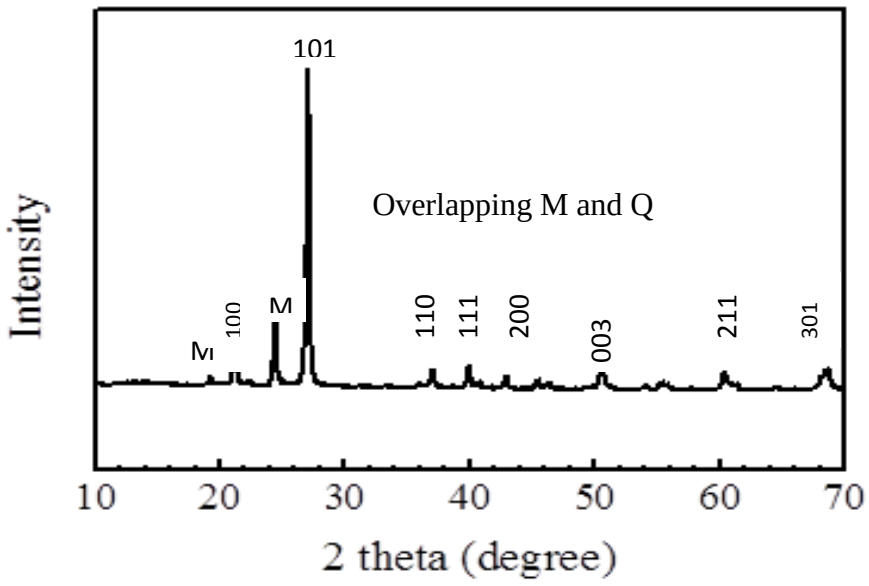

Fig. 15 X-ray diffraction patterns of the (addis zemen agate)

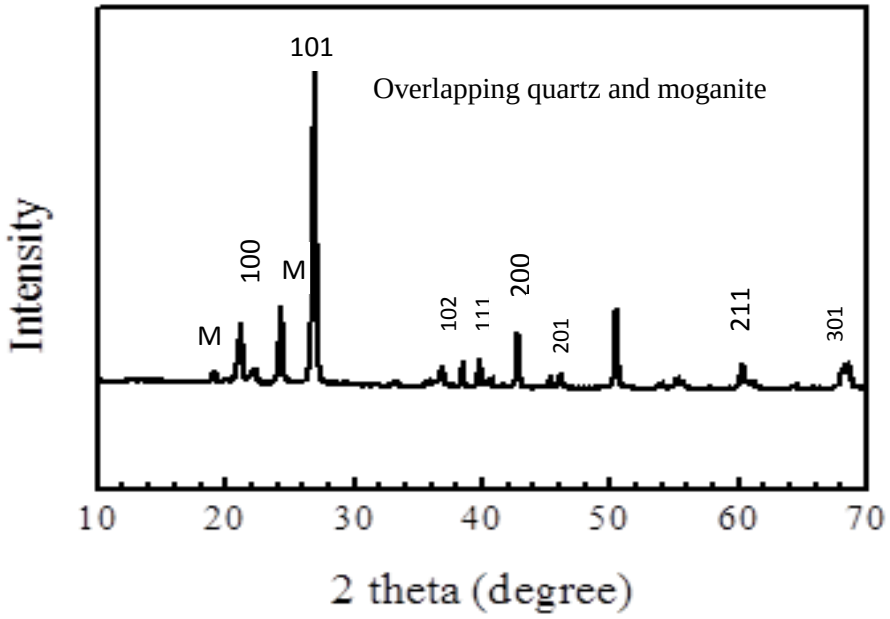

Fig. 16 X-ray diffraction pattern the (Bure agate)

An agate yielded powder XRD pattern is characterized by four broad reflections, the sharp and most intense diffraction peak is pointed at 2θ = 26.65°-27.00°, medium intense sharp peak observed around 2θ = 20.00°, 24.00° and 50.14°, broad peak at 2θ = 20.83° and 68.85° and there is also weaker reflection band which occur at 2θ = 55° and 64.00°. By using XRD the same result were obtained in [14, 32, and 36]. A sharp intense peak indicates highly ordered, more crystalline than that of medium as well as weak peaks. The main and sharp peak occurred at 2θ = 26.65° indicating the degree of order in agate structure and the broad peak at 2θ = 20.85°, 36.54°, 39.46°, 42.47°, 45.81°, 50.14°, 54.87°, 59.95° and 68.32° indicates the presence of microcrystalline quartz building phases, such as cryptocrystalline alpha-quartz called chalcedony, cryptocrystalline quartzine (called moganite). This demonstrate that the moganite silica phases are present at 2θ = below 20° and around 24° and additionally in the overlapped diffraction bands. The observed XRD patterns of the investigated natural gem-agate samples are comparable with the literature and standard x-ray diffraction powder pattern of silicon oxide (Quartz-low), α-SiO_2 in the table 5 below [36].

When we compare the peaks of the three samples sharp peak were observed in the Bellesa agate sample. This demonstrates the Bellesa agate sample is highly ordered crystalline than that of

Bure and Addis zemen agate sample. The Bure and addis zemen samples have similar peak intensity and this shows that the two samples have resemblance in crystalline order.

Table 5. Standard x-ray diffraction powder pattern Silicon Oxide (Quartz-low), α-SiO_2

[CAS registry no. 7631-86-9]

CuK α_1	λ= 1.540598Å temp 25±1° C Internal standard Si α = 5.43088Å		
d (Å)	I^{rel} σ =±1	h k l	2 θ(°)
4.257	22	1 0 0	20.85
3.342	100	1 0 1	26.65
2.457	8	1 1 0	36.54
2.282	8	1 0 2	39.46
2.237	4	1 1 1	40.29
2.127	6	2 0 0	42.47
1.9792	4	2 0 1	45.81
1.8179	14	1 1 2	50.14
1.8021	1L	0 0 3	50.61
1.6719	4	2 0 2	54.87
1.6591	2	1 0 3	55.33
1.6082	1L	2 1 0	57.24
1.5418	9	2 1 1	59.95
1.4536	1	1 1 3	64.00
1.4189	1L	3 0 0	65.76
1.3820	6	2 1 2	67.75
1.3752	7	2 1 2	68.13
1.3718	8	3 0 1	68.32

4.4 Flame atomic absorption spectroscopy analysis

The geochemical investigations of agates from their parent volcanic rocks and associated silicate mineralization represent an extensive analytical characterization of agates from localities around the world. Despite the different origin of the agate samples investigated, some common geochemical characteristics were observed. The trace element signature of most agate sample is characterized by FAAS. Concerning our study, we have characterized trace element signature of natural gem agate samples from Bellesa, addis zemen and bure using FAAS. The results of the investigated samples are given in table 6 below.

Table 6. The Mean concentration of trace element contents in natural gem agate sample

Agate sample	Concentration of metal in mg/L(ppm)						
Site	Ca	Mg	Mn	Cu	Fe	Zn	Cd
West Gojam	0.247	0.349	0.011	0.004	0.199	0.001	Nd
North Gondar	0.357	0.293	0.016	0.015	0.389	Nd	0.002
South Gondar	0.057	0.275	0.037	0.009	0.208	0.001	Nd

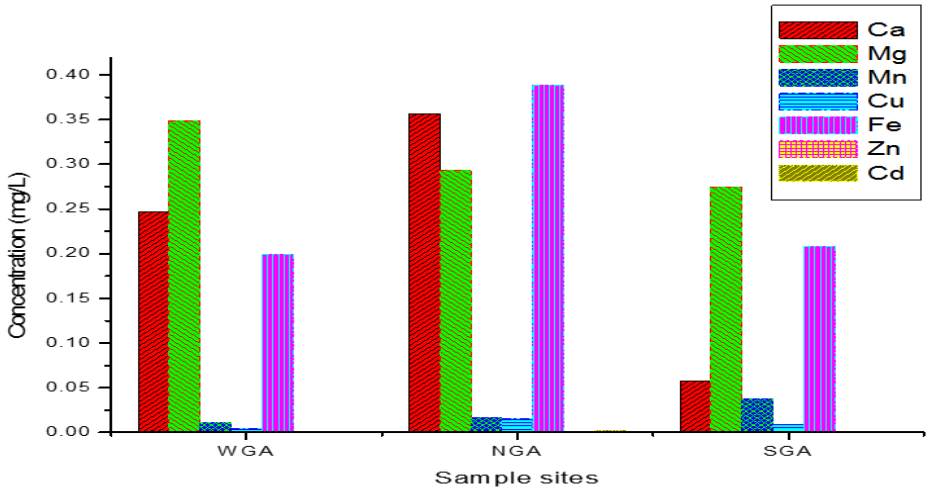

Fig. 17 Histogram comparing mean concentrations of metals in (WGA, NGA and SGA)

Trace element analyses of agates, quartz incrustations and associated parent volcanic rocks are carried out to obtain more information about the geochemistry of agates. Most trace elements show variations in their concentrations comparable to those seen in rock quartzes originating from different parent rocks. However, elevated concentrations were detected for those elements that are commonly contained within micro inclusions in the agate (Cu, Ca, Fe, Mn and Mg). They are frequently concentrated in colored agate bands, obviously acting as pigments [37]. In this study, the agate sample from WG and SG have a high content of magnesium (Mg) and less amount of copper (Cu) whereas the agate sample of NG has the high content of iron (Fe) and small amount of copper (Cu). The color of agate is mainly associated with the presence of transition metals in its composition. The color of NGA is brown red associated with high Fe content, SGA and WGA is a mixture of gray and white which is associated with high content of Ca and Mg. The most common solid inclusions found within the agate matrix include pyroxene, calcium rich plagioclase, and goethite, and magnesite, Mn and Cu compounds [32].

Further work

In view of the present results, some further directions of research appear manifest. As in all preliminary studies, results need to be confirmed by further analyses and also in order to provide complete study of the agate samples, additional instruments such as SEM, ICP and Raman spectroscopy should be used.

5 CONCLUSION

Agate samples were collected from North Gondar, South Gondar and West Gojam Zones in the Amhara National Regional State, Ethiopia. These samples were characterized using physical property measuring devices (Refractometer, heavy liquid method and "MOHS HARDNESS PENCILS") and Spectroscopic Techniques (FAAS, XRD and FT-IR). The performed physical property measurement had confirmed the correct identity of the agate samples. The data obtained by measuring the agate samples using spectroscopic techniques were comparable with studies conducted in different countries by different researchers. The performed physical analysis showed that the hardness value of Bure and Addis zemen agate are within the range of 6.5-7 and that of Bellesa is 7 (slightly harder than that of Bure and Addis zemen) but the refractive index and specific gravity of these investigated samples have similar value i.e., in between 1.53-1.54 and 2.4-2.7 respectively. The crystal structure were estimated using XRD studies was the Bellesa agate is highly crystalline than the two, trace and minor elements were determined using FAAS, and the major compositional elements and water contents were confirmed by FT-IR studies. Using the FAAS Spectroscopic technique, seven elements (Ca, Mg, Cd, Cu, Fe, Mn, and Zn) were measured. The FAAS result showed that the intensity of orange color (from yellow to orange to red to "chocolate"- brown) correlates with the large amount of Fe concentration and white color correlate with large amount of Ca concentration in the agate samples. It is also presented that the FT-IR spectroscopy could not discriminate between the difference color varieties of the studied agate samples. However, the presented FT-IR spectra data for agate samples have a significant contribution in their identification and characterization. This spectroscopic technique is important to identify their functional group in the agate formation. XRD patterns were used to determine mineralogical assemblage of host rocks. It helped to classify the base silica building components in to moganite, quartz and chalcedony. Generally by using these technique to compare three sample with other countries like Australia, turkey and morocco the Bellesa agate is hard more crystalline appreciated and comparable.

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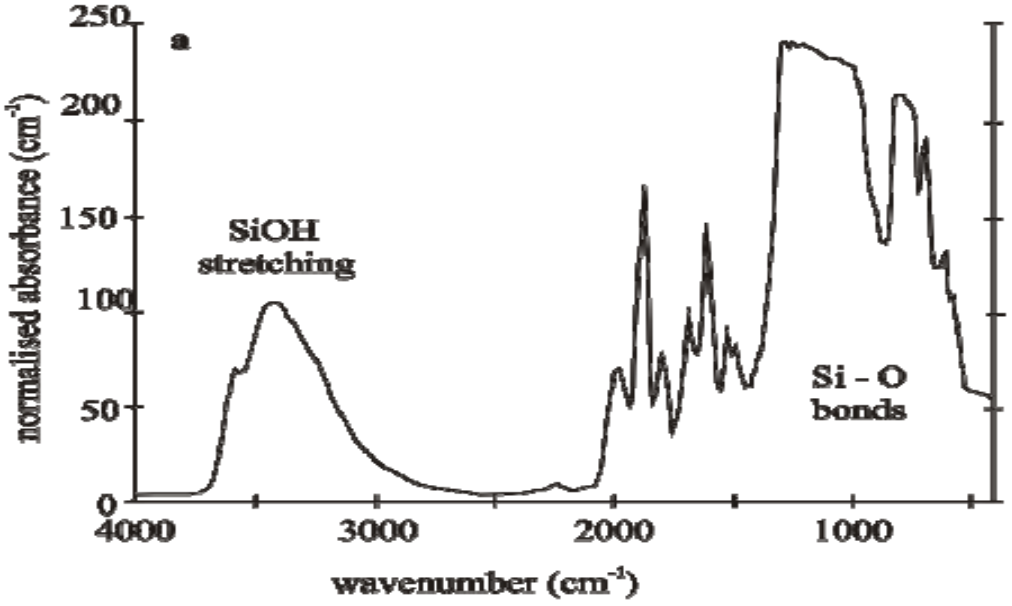
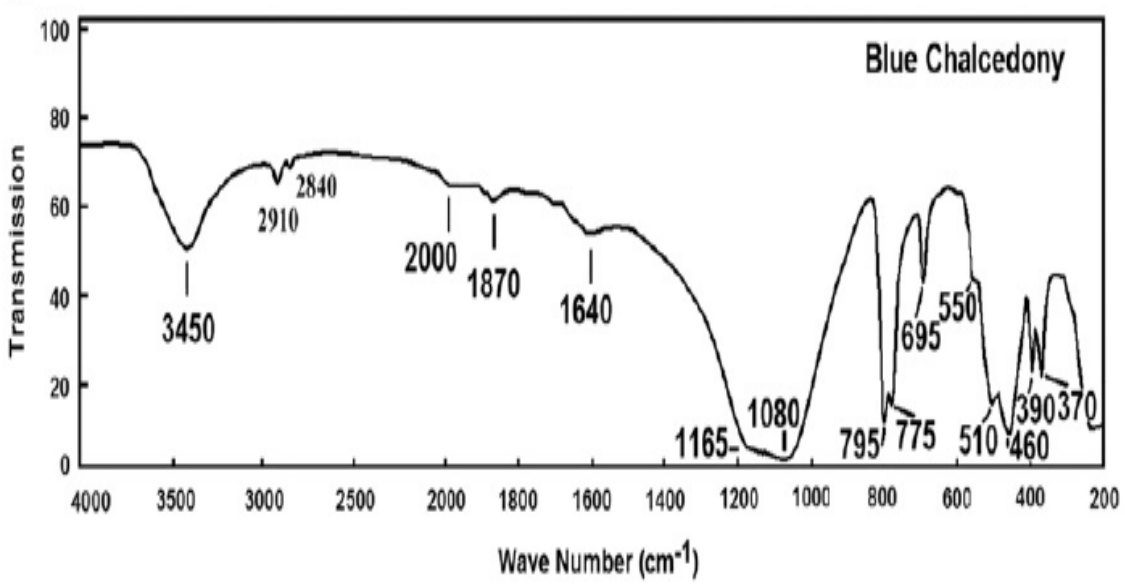
7 APPENDICES

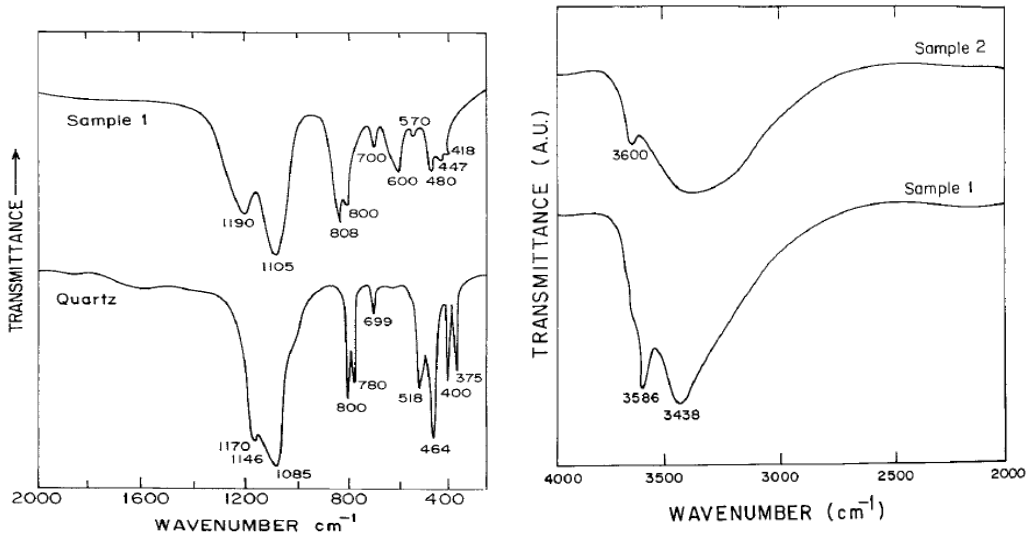
Appendix A. FT-IR Spectra of different agate samples from different countries from different literatures.



[33]

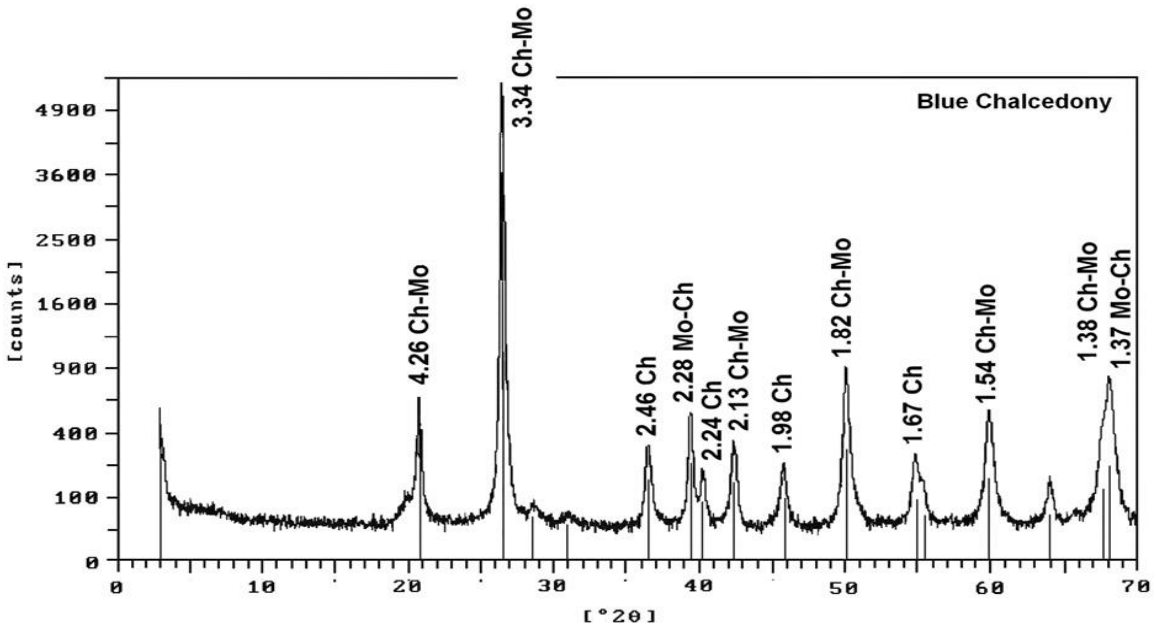


[34]

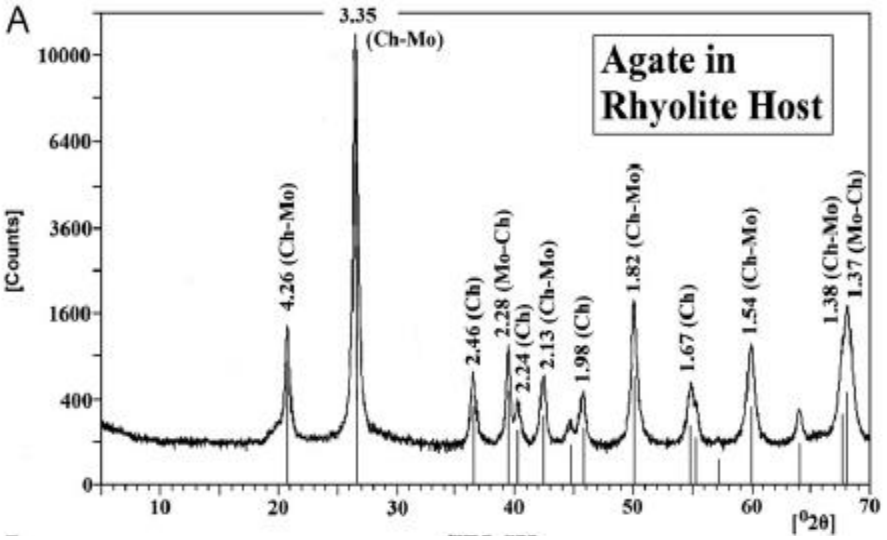


[35]

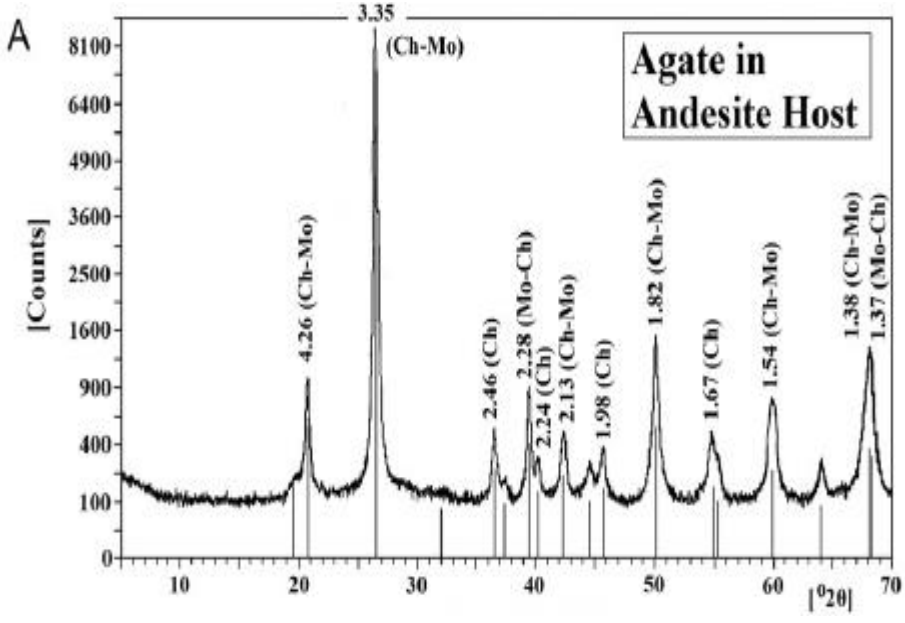
Appendix B. XRD patterns of different agate samples from different countries from different literatures.



[34]


A
3.35
(Ch-Mo)
Agate in
Rhyolite Host
[Counts]
10000
6400
3600
1600
400
0
4.26 (Ch-Mo)
2.46 (Ch)
2.28 (Mo-Ch)
2.24 (Ch)
2.13 (Ch-Mo)
1.98 (Ch)
1.82 (Ch-Mo)
1.67 (Ch)
1.54 (Ch-Mo)
1.38 (Ch-Mo)
1.37 (Mo-Ch)
10
20
30
40
50
60
70
[0 2θ]

[36]


A
3.35
(Ch-Mo)
Agate in
Andesite Host
[Counts]
8100
6400
4900
3600
2500
1600
900
400
100
0
4.26 (Ch-Mo)
2.46 (Ch)
2.28 (Mo-Ch)
2.24 (Ch)
2.13 (Ch-Mo)
1.98 (Ch)
1.82 (Ch-Mo)
1.67 (Ch)
1.54 (Ch-Mo)
1.38 (Ch-Mo)
1.37 (Mo-Ch)
10
20
30
40
50
60
70
[0 2θ]

[36]